APPLICATION

FOR

UNITED STATES OF AMERICA

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SPECIFICATION

TO ALL WHOM IT MAY CONCERN:
Be it known that We,

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have invented certain improvements in

"BLUE EMITTING TRIS (8-OXOQUINOLINE) ALUMINUM (III) (Alq₃)"

of which the following description in connection with the accompanying drawings is a specification, like reference characters on the drawings indicating like parts in the several figures.

The present invention relates to the isolation of the facial stereoisomer of the electroluminescent molecule tris(8-oxoquinoline)aluminum(III) (Alq_3), its mass production and its characterization in solution and in the solid state.

BACKGROUND OF THE INVENTION

The first highly efficient and low-voltage-driven organic electroluminescent devices (OLED), have been reported by Tang and Van Slyke (1), and were based on Alq_3. Fifteen years later, Alq_3 is still a key electroluminescent compound, widely used in commercial devices and has become the prototype of a whole class of materials used as active layers in electroluminescent devices. Recently, significant improvements in device efficiency and stability have been obtained (2-6), and many efforts have been spent in order to extend and modify the typical green emission of Alq_3–based OLEDs, using multilayers structures and chemical doping (7-9).

Tris-chelated octahedral complexes (such as Alq_3) can exist in the fac or mer isomeric forms. In the case of trisoxoquinoline complexes (Mq_3), only mer stereoisomers have been reported and characterized. The only reported example of a non-mer isomer is the Sbq_3 complex (10) which, however, is not octahedral, thanks to the presence of a stereochemically active lone pair.

In the Alq_3 molecule, the possible existence of different geometrical isomers is still an unresolved issue. Despite of the many investigation efforts during several years (11-14), the facial stereoisomer of Alq_3 has never been directly observed. Invariably, spectroscopic studies on matrix-isolated molecules, solutions and polymorphic crystal phases (13, 15) have evidenced the existence of the green-emitting mer isomer only. Curioni et al. have theoretically predicted through computational models (16) that the fac isomer is less stable ($\Delta E \approx 4$ kcal/mol) than the mer isomer and that it possesses a 0,3 eV higher energy gap (HOMO-LUMO), with a dipolar moment of 7 Debye (16).

Mer-Alq$_3$ crystallizes as α e ß phases (and in a number of clathrates), whose optical properties are determined by the nature of the π-π intramolecular contacts (15). In addition, partial crystallographic information on two phases, generated at elevated temperatures, called γ e δ, has been reported (15, 17).

SUMMARY OF THE INVENTION

The main task of the present invention in the isolation of the facial isomer of Alq$_3$ (later shown to be a blue-emitting species) both in solution and in the solid state.

The aim of the present invention is to provide a procedure which allows to prepare large quantities of the blue-luminescent γ e δ phases, both containing the elusive facial isomer of Alq$_3$.

Another aim of the present invention in to provide a method capable to stabilize the facial isomer of Alq$_3$ in solution.

One further aim of the present invention is to provide a method for obtaining blue-emitting thin films of Alq$_3$.

Another aim of the present invention is to provide blue-emitting electroluminescent devices based on Alq$_3$.

The above-mentioned aims and other aims which will become evident from the following descriptions have been reached through the solid-state synthesis of the facial isomer (γ-Alq$_3$) upon heating α-Alq$_3$ at temperatures higher than 350°C, but lower than 420°C (typically 390 °C), followed by its transformation into the δ-Alq$_3$ phase by suspending the product obtained by heating in organic solvents (for example, acetone) and maintaining the suspension at room temperature.

Typically, heating of solid phase α-Alq$_3$ is performed with a temperature gradient of 10°C/min in the 50 to 350°C temperature range.

Preferably, subsequent heating in the 350°C to 390-420°C range is performed with a temperature gradient of 1°C/min.

As a further aspect, the present invention offers a procedure for the preparation of thin films of δ e γ-Alq$_3$, which comprises the preliminary

preparation of δ e γ-Alq₃ solutions (for example, in CHCl₃) at temperatures lower than −10°C, followed by the deposition of a thin layer of such solution on a substrate and followed by the fast solvent evaporation.

Solvent evaporation can also be accomplished at room temperature.

5   In the following, we report the direct observation of the fac isomer of the Alq₃ molecule by NMR spectroscopy as well as the key steps for its isolation and massive production, through a solid-solid reaction starting from the commercial (α-Alq₃) material. The optical emission properties of the fac isomer in solution, both in polycrystalline powders and films, are compared

10   with those of the mer isomer. The crystal structure of the fac isomer in the γ and δ phases has been determined by X-ray powder diffraction methods (XRPD), which evidences the absence of π-π intermolecular contacts between oxyquinoline ligands.

The facial (fac) isomer shows a blue emission rather different from the

15   green light emission typical for the meridianal (mer) isomer.

A phase transformation diagram and a production method for the fac isomer is provided, starting from powders of the mer isomer.

The fac isomer crystallizes in two polymorphic species, the structures of which have been resolved by ab-initio X-ray powder diffraction methods. Both

20   crystal phases show blue emission γ and δ-Alq₃ are the only known examples of Mq₃ species containing, in the solid state, the fac isomer.

The solution of the longstanding issue of the Alq₃ isomery opens the way to the development of blue-emitting electroluminescent devices based on Alq₃.

BRIEF DESCRIPTION OF THE DRAWINGS

25   The invention is described with more detail with the aid of the following figures:

figure 1: phase transformation diagram for Alq₃,

figure 2: ¹H NMR spectra (8-9 ppm range, at different temperatures) of δ -Alq₃ dissolved in CDCl₃.

30   figure 3: top: photoluminescence spectra of fac and mer Alq₃

solutions, excited by an ultraviolet laser beam; bottom: photoluminescence spectra of α- e γ-Alq₃ in the form of films, obtained from solutions and illuminated by a UV laser beam. The inserts show the molecular structures of the fac and mer isomers.

5   figure 4: crystal packing of the triclinic crystals of δ-Alq₃, viewed down [001]. At this drawing resolution, the crystal structure of the trigonal γ-Alq₃ phase is rather similar.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Alq₃ Isomery. Polycrystalline powders of α-Alq₃ are transformed
10   predominantly into the γ phase upon heating at a temperature between 390°C and 420°C at atmospheric pressure. We discovered that a few drops of liquid acetone favor the transformation of the γ phase into the δ phase, while seeding of supersaturated solutions of mer-Alq₃ with nuclei of γ (or δ) do not afford the δ phase. These experimental evidences have suggested the
15   existence of a different Alq₃ isomer and prompted for new systematic spectroscopic and structural analyses. The results of these investigations are reported in the phase transformation diagram depicted in figure 1, which shows the existence of four distinct solid phases for (unsolvated) Alq₃, based on the existence of two different stereoisomers. The fac isomer can only be
20   obtained by a solid state reaction (blue arrow). However, diluted solutions of the fac isomer can be obtained from the γ (or δ) phases at low temperatures, given that it is kinetically stable below −10°C.

At room temperature, independently from the starting material (α phase, γ phase or δ phase), solution ¹H and ¹³C-NMR experiments have
25   shown that mer-Alq₃ is the only present species. However, upon suspending solid γ- or δ-Alq₃ powders in CDCl₃ at a temperatures of −50°C, ¹H-NMR signals show the existence of only the fac-Alq₃ isomer. This neatly shows that γ- and δ-Alq₃ contain the fac isomer, which is kinetically stable, in the solid state, at room temperature.

30   From the spectra shown in figure 2 one can observe, at low temperatures,

the absence of the H2 signals near δ 8,8 ppm, which, coupled with the fact that only the (magnetically equivalent) H4 nuclei are observed, shows that only the fac isomer is present. The increase of the signal-to-noise ratio observed upon heating the solution is a manifestation of the progressive

5 transformation of the fac isomer into the more soluble mer-Alq₃.

Moreover, the spectra reported in figure 2 show that such isomerization begins at temperatures above ca. −10°C. It is worth noting that solutions prepared at room temperature from δ-Alq₃ only contain the mer isomer as a result of the rapid fac to mer transformation.

10 The photoluminescence spectra of solutions of mer- and fac-Alq₃ are shown in figure 3 − top. The fac-Alq₃ solution has been prepared by dissolving powders of the γ or δ phases in CHCl₃ at −50°C. The photoluminescence of fac-Alq₃ in solution at −50°C is centered at 2,59 eV and has a brilliant blue color. The spectral position of the photoluminescence

15 does not change at temperatures below −10°C, while at higher temperatures it progressively shifts towards lower energies. It has been observed that the spectral emission maximum constantly decreases with increasing temperature, reaching a minimum value of 2,36 eV (green) at room temperature. This is in agreement with the NMR spectroscopic results, which

20 show conversion of fac into mer at temperatures above −10°C. From the photoluminescence spectra, we found that the transformation is complete after a few hours at room temperature.

Thus, the photoluminescence spectral emission features provides a characteristic fingerprint of each isomer.

25 **Solid-solid Transformations.** On the basis of ab-initio quantomechanical computations, in the gas phase, the mer isomer is ca. 4 kcal/mol more stable than the fac isomer, but has significantly lower dipolar moment (4,1 vs. 7,1 Debye). If we assume that this also holds in solution, we can easily explain why the solution chemistry of Alq₃ is dominated by the mer isomer: in other

30 words, one cannot obtain solutions of fac-Alq₃ through a chemical process in

solution. These results are fully in agreement with the long known ^{1}H-NMR experiments, which revealed the mer isomer only at all investigated temperatures. (11). Upon increasing the temperature in the solid state, small energy differences can be overcome by entropic contributions, eventually assisted by cavity effects or a more efficient crystal packing. Indeed, the solid state transformation of mer into fac, starting from the α phase, occurs only near 390°C. Surprisingly, the γ phase, which is indefinitely stable in the solid state, can be easily transformed into the δ phase, at room temperature, if a few drops of liquid acetone are added. The acetone molecules give a limited mobility to the fac molecules which, well before isomerization, crystallize as the denser and more stable δ phase.

Crystal data for γ-Alq$_3$: $C_{27}H_{18}AlN_3O_3$, molar weight 409,43 g/mol, trigonal, space group P-3, a=14.3807(6), c=6.2107(4)Å; V=1112.3(1)Å^3, Z=2; ρ_c=1.371 g/cm^3; R_{wp} and R_p: 0.133 and 0.102 for 3501 data collected in the 5<2θ<75° range. R_{Bragg} 0.037.

Crystal data for δ-Alq$_3$: $C_{27}H_{18}AlN_3O_3$, molar weight 409,43 g/mol, triclinic, space group P-1, a=14.44479(9), b=13.2620(7); c=6.1887(4) Å; α =95.865(5); β =88.613(5); γ =113.922(4)°; V=1078.1(1)Å^3, Z=2; ρ_c=1.415 g/cm^3; R_{wp} and R_p: 0.161 and 0.124 for 3501 data collected in the 5<2θ<75° range. R_{Bragg} 0.061.

Crystals of γ-Alq$_3$ belong to the trigonal space group P-3. Fac-Alq$_3$ shows C_3 symmetry. δ-Alq$_3$ is triclinic, space group P-1, thus its three oxoquinoline ligands are crystallographically independent. Figure 4 shows the pseudo-trigonal crystal packing of δ-Alq$_3$. The crystal structure of γ-Alq$_3$ is similar, with the molecules lying on threefold crystallographic axes of the trigonal space group P-3. The two phases are correlated by a proper group-subgroup relationship, since the δ phase can simply be obtained by removing the threefold axes of the γ phase, but maintaining all inversion centers. The small differences in the crystal packings of γ- and δ-Alq$_3$ are evident in their Raman spectra, which contain the same intramolecular phonon modes, but different

lattice modes (20). The optical emission spectra of γ- and δ-Alq$_3$ are identical, as later discussed.

α-Alq$_3$ (15), γ- and δ-Alq$_3$ possess similar lattice parameters, thus showing that different stereoisomers can adopt similar packing modes. The common motif is the presence of chiral columns of [Alq$_3$]$_∞$, parallel to the c axis, pseudotrigonally packed in the ab plane. In all these phases, thanks to their centrosymmetric nature, molecules of (±)Alq$_3$ and the columns of opposite chirality coexist in an equimolar ratio.

Solid state optical properties. The possibility of preparing stable blue emitting thin films of Alq$_3$ derives from the comprehension of the Alq$_3$ isomery and from the phase transformation diagram. The availability of stable solutions of fac-Alq$_3$ allows the preparation of films which maintain the characteristic blue emission of the fac-Alq$_3$ isomer. Figure 3 – bottom – shows films obtained by deposition of a solution of fac-Alq$_3$ and of a solution of mer-Alq$_3$ on quartz substrates. At low temperatures, the fac to mer transformation is relatively slow and allows the stabilization of the fac isomer in the solid phase after solvent evaporation, even when the substrate is kept at room temperature. Figure 3 – bottom – shows the photoluminescence spectra measured on polycrystalline powders of α-Alq$_3$ (green) and δ and γ-Alq$_3$ (blue) at 4K. As mentioned above, there is no significant difference between the photoluminescence spectra of the γ and δ phases. The spectra of α- and γ-Alq$_3$ clearly show the same vibronic progression due to the bending mode at 525 cm^{-1} (21) which, in both cases, is described by a Huang-Rhys factor of ca. 2,6. This indicates that in both isomers the same strong electrion-phonon coupling is present in the radiative electronic transition.

The photoluminescence spectra of the thin films of the mer and fac isomer are similar to those of the powders of α and γ (or δ) but are red-shifted and, even at low temperatures, do not show the vibronic progression. This behavior is typical in thin films of Alq$_3$ and has been interpreted in the past as a consequence of the coexistence of the two isomers (2, 16). In the light of

the results here reported, the amorphous nature of the thin films of Alq_3 is more likely attributed to the polymorphism, rather to the racemic nature, of Alq_3.

The discovery of blue emitting stable phases of Alq_3 allows the
5 fabrication of blue emitting efficient OLEDs based on Alq_3. This, together with a deeper knowledge of the optical and electronic properties of Alq_3, may allow the use of a unique active material in color visualization devices of the RGB (red, green, blue) type.

NMR Spectroscopy: α-Alq_3 can easily be dissolved in a number of
10 organic solvents; differently, δ-Alq_3 shows much lower solubility. In a first series of NMR experiments, powders of α-Alq_3 and δ-Alq_3 were dissolved in $CDCl_3$ at room temperature. The ^1H and ^{13}C NMR spectra have been collected on a 400 MHz Bruker NMR AVANCE instrument.

The room temperature ^1H-NMR spectrum of mer-Alq_3 fully agrees with
15 that reported in (18). The molecular aggregation in solution, originally observed through fluorescence spectroscopy (15) has been confirmed from the concentration dependent chemical shifts of the "external" protons, particularly of H4. A peculiarity of this spectrum is the anomalous lowering (1,5 ppm) of the chemical shift of one of the three H2 atoms. This is due to
20 the unique intramolecular environment of this H2 atom, pointing toward an adjacent aromatic ring. This information is of high relevance in the interpretation of the ^1H NMR spectrum of the fac-Alq_3 isomer at $-50°C$. Indeed, the stereochemistry of fac-Alq_3 requires that all H2 atoms feel diamagnetic ring currents.

25 In a second series of NMR experiments, solid δ-Alq_3 has been cooled to liquid nitrogen temperature in an NMR tube. $CDCl_3$ has been added and the temperature has been raised to $-50°C$ at controlled rate in about 30 minute time. A series of ^1H NMR spectra has been measured at this temperature, which demonstrated the absence of molecular isomerisation even after a few
30 hours. Further spectra were subsequently collected upon increasing the

temperature by 10° intervals, up to room temperature. 10 minutes delays have been given after each spectrum, in order to thermally stabilize the system.

The fac-Alq$_3$ isomer shows a simpler ^{1}H NMR spectrum, due to its C3 symmetry. It consists of two multiplets centered near δ 8,36 ppm (H4) and δ
5   7,52 ppm (H6) and of many severely overlapped peaks, in the 7,1 to 7,4 ppm range (H2, H3, H5 e H7). All resonances of the H2 atoms are shifted to high fields, just as the unique H2 atom of mer-Alq$_3$ (δ 7,22 ppm, see (18)).

Powder X-ray diffraction analysis: indexing of the diffraction pattern of γ-Alq$_3$ confirmed the reported trigonal metrics and gives better figures of
10 merit [a = 14.364, c = 6.208 Å; M(22) = 42, F(22) = 56 (0,009, 43)]. On the basis of a complete Rietveld analysis, the correct trigonal space group in not P-31c (15) but P-3 (00l reflections being obscured by accidental overlap). We note the original assignment of γ-Alq$_3$ as based on the mer isomer was tentatively presented using a low quality XRPD pattern (not allowing a
15 complete modeling by the Rietveld technique), together with the consideration that in the sublimed powders only mer-Alq$_3$ was present. The complete Rietveld analysis here reported determines in a definitive manner the molecular (fac) and crystal line structure of γ-Alq$_3$. Indexing of the diffraction pattern of the δ polymorph leads to a triclinic cell [a = 14.503,
20 b = 13.288, c = 6.208 Å; α = 95,9; ß = 89,7; γ = 114,0; M(23) = 21, F (23) = 53 (0,009, 47)]. The structure resolution of γ- and δ-Alq$_3$ has been performed by the simulated annealing technique (Bruker AXS 2000; Topas V2.0.). The final refinement of the structural models of biphasic mixtures have been performed on two different sets of data (Γ and Δ, rich,
25 respectively, in γ- and δ-Alq$_3$,) collected in the 5<2θ<75° range, with step size Δ2θ =0,02°, t=60 (Γ) or 100 (Δ) s step^{-1}. Both in the solution and in the refinement steps we used oxyquinoline fragments of ideal geometry, hinged about the Al atom through flexible restraints [on the intramolecular contacts 1,2 Al/X and 1,3 X/X (X = N,O) of a fac stereoisomer]. The XRPD traces
30 have been collected on a conventional powder diffractometer (Philips

PW1820) equipped with Soller slits, a secondary beam graphite monochromator, and Cu-Kα radiation, λ= 1.5418 Å, 40 KV, 40 mA.

The following examples are given for illustration but not limitation of the present invention.

5 **Examples**

Example # 1

Preparation of γ-Alq$_3$ (polycrystalline powders): commercial α-Alq$_3$ is heated to 395°C using a temperature gradient of 10°C/minute in the 50-350°C range and of 1°C/minute between 350°C and 395°C. After

10 maintaining the system at this temperature for some minutes, is its rapidly cooled down to room temperature. The XRPD analysis show that the resulting powders, of dark yellow color, consist of a mixture of the γ-Alq$_3$ and δ-Alq$_3$ phases. On using 15 mg of α-Alq$_3$ powders, the γ-Alq$_3$/δ-Alq$_3$ ratio is close to 10/1; such ration is not significantly modified by an increase

15 of the heating rate up to 10°C/minute or by a decrease of the cooling rate, down to 1°C/minute. Moreover, this ratio remains unchanged by heating at the maximum pre-sublimation temperature of 410°C. The use of larger amounts of the starting material (grams), however, was found to typically afford lower γ-Alq$_3$/δ-Alq$_3$ ratios.

20 **Example # 2**

Preparation of δ-Alq$_3$ (polycrystalline powders): γ-Alq$_3$, prepared as described in the Example # 1 and thus containing already small quantities of δ-Alq$_3$, is suspended in acetone for 15 hours at room temperature with occasional stirring. Through centrifugation, the resulting light yellow powder

25 is then recovered. The XRPD analysis shows the presence of (almost pure) δ-Alq$_3$ phase, accompanied by less than 4% residual γ-Alq$_3$. Neither the solvent volume nor the γ-Alq$_3$/δ-Alq$_3$ ratio in the starting powders have any influence on the γ-Alq$_3$/δ-Alq$_3$ ratio in the final mixture.

The disclosures in Italian Patent Application No. MI2002A001330 from

30 which this application claims priority are incorporated herein by reference.

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